Abstract

Air pollution in coastal urban areas remains one of the most serious environmental challenges in the State of California. Urban airshed models, which have been the basis of the development of air pollution mitigation strategies for many years, depend on the accurate description of the relevant chemical mechanisms. Therefore, it is crucial to determine whether the current chemistry in these models is complete, or whether new species and their reactions should be included. The primary goal of this project was to provide experimental evidence for the presence of reactive halogens, reactive halogen precursors, and halogen chemistry in coastal air masses and in the Los Angeles Basin to determine whether halogen chemistry should be included in current urban airshed models of Southern California.

The results of our field experiment at Zuma Beach, Malibu, in October 2006 clearly showed that halogens are present in coastal air upwind of Los Angeles, and that halogen chemistry is occurring. Evidence for chlorine chemistry was found through the observation of up to 12 ppt of Cl_2 and the presence of the chlorine reaction product chloroacetone. Bromine chemistry was found to be less important most of the time. However, sporadic observations of up to 10 ppt of Br_2 deserve further attention. I_2 levels remained below 1 ppt due to its rapid photolysis and the nocturnal off-shore winds. However, observations of several ppt of IO and OIO are proof that iodine chemistry is also occurring.

Macrocystis pyrifera, commonly known as Giant or Iodine Kelp, which is the predominant macroalgae species at the Southern California coast, appears to be the dominant biological source of iodine, and most likely also of bromine. Single particle composition analysis revealed the presence of processed sea salt aerosol at Malibu, indicating that sea salt aerosol is the most likely chemical source of reactive chlorine.

Modeling studies by the UCLA group and comparison with published studies showed that chlorine and iodine chemistry can lead to an increase of ozone levels of 8% (4.5 ppb increase at a 55 ppb base value) in the morning in coastal urban areas in California. The afternoon ozone peak of 76 ppb, on a moderately polluted day, increased by 4% or 3.5 ppb. The presence of halogens also increases OH concentrations by up to 10% and changes the NO/NO_2 ratio. The observation of N_2O_5 shows that the formation of $ClNO_2$ should be considered as an important source of reactive chlorine. Because chlorine and iodine chemistry are linked, the inclusion of iodine chemistry increases chlorine levels in our model and leads to enhanced formation of ozone away from the coastal zone. Models of halogen chemistry should thus always include all three halogen species: chlorine, bromine, and iodine. It should be noted that the model calculations in this project were intended to give more insights into the chemistry of halogens and ozone, rather than to provide an accurate quantification on the ozone levels in the LA-Basin.

The results of our study also revealed a lack in our understanding of the chemistry forming Cl_2 at night, and suggested the importance of as-yet-unidentified iodine reactions. While we have identified kelp as an important source of iodine and probably also of bromine, we cannot estimate the total amount of halogens that are emitted from this source along the California coast.

Our results clearly show that halogen chemistry will impact atmospheric chemistry in Southern California. However, the uncertainties in the chemistry and the sources of halogens make it challenging to give an accurate quantitative assessment of the impact of halogens on the formation of ozone and particles in the Los Angeles Basin. Further research is needed to close the gaps in our understanding of halogen chemistry in polluted coastal areas.